

**PROCESS FOR THE HYDROFORMYLATION OF ETHYLENICALLY
UNSATURATED COMPOUNDS**

The present invention relates to the hydroformylation of ethylenically unsaturated compounds by reaction with carbon monoxide and hydrogen in the presence of a catalyst system.

The carbonylation and hydroformylation of ethylenically unsaturated compounds using carbon monoxide in the presence of hydrogen and a catalyst comprising a group VIII metal, example, rhodium, and a phosphine ligand, example an alkyl phosphine, cycloalkyl phosphine, aryl phosphine, pyridyl phosphine or bidentate phosphine, has been described in numerous patents and patent applications.

WO 96/19434 disclosed that a particular group of bidentate phosphine compounds can provide stable catalysts in carbonylation reaction systems, and the use of such catalysts leads to reaction rates which were significantly higher than those previously disclosed.

WO 01/68583 discloses carbonylation processes for higher alkenes of three or more carbon atoms.

WO 02/76996, for example, discloses a method for producing diphosphines, and their use as co-catalyst for hydroformylating olefins. WO 02/20448 similarly discloses the preparation of arylphosphines for the rhodium-catalysed hydroformylation of alkenes.

Although catalyst systems have been developed which exhibit reasonable stability during the hydroformylation process and permit relatively high reaction rates and regioselectivity between linear and branched aldehyde products, there still exists a need for alternative and/or improved catalyst systems. Suitably, the present invention aims to provide an alternative and/or improved catalyst for hydroformylating ethylenically unsaturated compounds. Moreover, the present invention aims to provide solvents which improve the performance of the catalyst system.

Surprisingly, it has been found that improved selectivity of the linear aldehyde product compared to the branched aldehyde product can be obtained than by using comparative catalyst systems of the prior art.

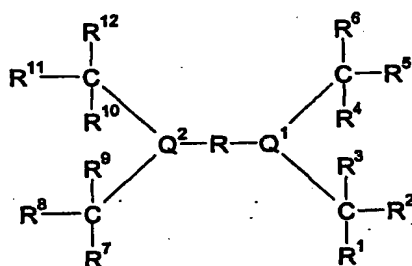
According to the present invention there is provided a process for the hydroformylation of ethylenically unsaturated compounds, as set forth in the appended claims. Preferred features of the invention will be apparent from the dependent claims, and the description. Also according to the present invention there is provided a catalyst system, a hydroformylation reaction catalyst system, a reaction medium, a hydroformylation reaction medium, use of a catalyst system, use of a reaction medium, and a process for preparing a catalyst system and reaction medium, as set forth hereinafter and in the appended claims.

According to the first aspect of the present invention there is provided a process for the hydroformylation of ethylenically unsaturated compounds, which process

comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

- a) a metal of Group VIII or a compound thereof; and
- b) a bidentate phosphine of general formula (Ia)

(Ia)



wherein R is a covalent bridging group;

R¹ to R¹² each independently represent hydrogen, lower alkyl, aryl or Het, preferably, lower alkyl, aryl or Het;

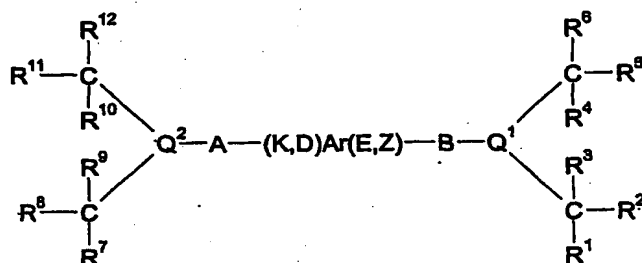
Q¹ and Q² each independently represent phosphorus, arsenic or antimony and in the latter two cases references to phosphine or phosphorus above are amended accordingly,

the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

Such a process is referred to hereinafter as "the process of the invention". The process of the invention includes the embodiments set out hereinafter.

In one set of embodiments, the group R in formula (Ia) may represent an alkylene bridging group, preferably, a lower alkylene.

In another and preferred set of embodiments, the bridging group R may be defined as $-A-(K,D)Ar(E,Z)-B-$, such that general formula (Ia) becomes general formula (I),
(I)



wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, or $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro,

OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$,
 $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$;

R^1 to R^{18} each independently represent hydrogen, lower alkyl, aryl, or Het, preferably, lower alkyl, aryl or Het;

R^{19} to R^{27} each independently represent hydrogen, lower alkyl, aryl or Het;

Q^1 , Q^2 and Q^3 (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly.

Preferably, when K, D, E or Z represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, the respective K, D, E or Z is on the aryl carbon adjacent the aryl carbon to which A or B is connected or, if not so adjacent, is adjacent a remaining K, D, E or Z group which itself represents $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$.

Preferably, R^1 to R^{18} each independently represent lower alkyl or aryl. More preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, C_1 - C_6 alkyl phenyl (wherein the phenyl group is optionally substituted as defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein). Even more preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, which is optionally substituted as defined herein. Most preferably, R^1 to R^{18} each represent non-substituted C_1 to C_6 alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

Alternatively, or additionally, each of the groups R^1 to R^3 , R^4 to R^6 , R^7 to R^9 , R^{10} to R^{12} , R^{13} to R^{15} or R^{16} to R^{18} together independently may form cyclic structures such as 1-norbornyl or 1-norbornadienyl. Further examples of composite groups include cyclic structures formed between R^1 to R^6 , R^7 to R^{12} , and R^{13} to R^{18} . Alternatively, one or more of the groups may represent a solid phase to which the ligand is attached.

Moreover, at least one $(CR^xR^yR^z)$ group attached to Q^1 and/or Q^2 , i.e. $CR^1R^2R^3$, $CR^4R^5R^6$, $CR^7R^8R^9$, or $CR^{10}R^{11}R^{12}$, may instead be congressyl or adamantyl, or both groups defined above as $(CR^xR^yR^z)$ attached to either or both Q^1 and/or Q^2 , may, together with either Q^1 or Q^2 as appropriate, instead form an optionally substituted 2-phosphatricyclo[3.3.1.1^{3,7}]decyl group or derivative thereof. However, in this particular set of embodiments, i.e. when the bridging group is defined as $-A-(K,D)Ar(E,Z)-$, if any $(CR^xR^yR^z)$ groups are defined as per this paragraph, they are preferably congressyl or adamantyl, more preferably non-substituted adamantyl or congressyl, most preferably a non-substituted adamantyl group.

In a particularly preferred embodiment of the present invention R^1 , R^4 , R^7 , R^{10} , R^{13} and R^{16} each represent the same lower alkyl, aryl or Het moiety as defined herein, R^2 , R^5 , R^8 , R^{11} , R^{14} and R^{17} each represent the same lower alkyl, aryl or Het moiety as defined herein, and R^3 , R^6 , R^9 , R^{12} , R^{15} and R^{18} each independently represent the same lower alkyl, aryl or Het moiety as defined herein. More preferably R^1 , R^4 , R^7 , R^{10} , R^{13} and R^{16} each independently represent the same C_1 - C_6 alkyl, particularly non-

substituted C₁-C₆ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; R², R⁵, R⁸, R¹¹, R¹⁴ and R¹⁷ each independently represent the same C₁-C₆ alkyl as defined above; and R³, R⁶, R⁹, R¹², R¹⁵ and R¹⁸ each independently represent the same C₁-C₆ alkyl as defined above. For example: R¹, R⁴, R⁷, R¹⁰, R¹³ and R¹⁶ each represent methyl; R², R⁵, R⁸, R¹¹, R¹⁴ and R¹⁷ each represent ethyl; and, R³, R⁶, R⁹, R¹², R¹⁵ and R¹⁸ each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R¹ to R¹⁸ group represents the same lower alkyl, aryl, or Het moiety as defined herein. Preferably, each R¹ to R¹⁸ represents the same C₁ to C₆ alkyl group, particularly non-substituted C₁-C₆ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. Most preferably, each R¹ to R¹⁸ represents methyl.

In the compound of formula (I), preferably each Q¹, Q² and Q³ (when present) is the same. Moreover, in a compound of formula (Ia), preferably Q¹ and Q² are the same. Most preferably, each Q¹, Q² and Q³ (when present) represents phosphorous.

Preferably, in the compound of formula (I), A, B and J (when present) each independently represent C₁ to C₆ alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Moreover, in the compound of formula (Ia), R (when alkylene) represents C₁ to C₆ alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Preferably, the lower alkylene groups which A, B and J

(when present) represent are non-substituted. A particular preferred lower alkylene which A, B and J may independently represent is $-\text{CH}_2-$ or $-\text{C}_2\text{H}_4-$. Most preferably, each of A, B and J (when present) represent the same lower alkylene as defined herein, particularly $-\text{CH}_2-$. Particularly preferred lower alkylens which R represents are substituted or non-substituted and may be selected from ethylene ($-\text{C}_2\text{H}_4-$), and substituted variants thereof, propylene ($-\text{C}_3\text{H}_6-$), and substituted variants thereof, and butylene ($-\text{C}_4\text{H}_8-$), and substituted variants thereof, and wherein such substitution may be on any, some or all of the carbon atoms of the lower alkylene and such substitution may be with lower alkyl groups. More preferably, the lower alkylens which R represents are substituted or non-substituted ethylene or propylene, most preferably, substituted or non-substituted propylene.

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-\text{J}-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$, K, D, E or Z represents hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E or Z represent hydrogen, phenyl, C_1 - C_6 alkylphenyl or C_1 - C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Most preferably, K, D, E or Z represents hydrogen.

Preferably, in the compound of formula (I) when K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, K, D, E and Z each independently represent hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E and Z each independently represent hydrogen, phenyl, C_1 - C_6 alkylphenyl or C_1 - C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Even more preferably, K, D, E and

Z represent the same substituent. Most preferably, they represent hydrogen.

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, each of K, D, E and Z represent the same group selected from hydrogen, lower alkyl, aryl, or Het as defined herein; particularly hydrogen or C_1-C_6 alkyl (more particularly unsubstituted C_1-C_6 alkyl), especially hydrogen.

Preferably, in the compound of formula (I) when two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring, then the phenyl ring is optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined herein). More preferably, the phenyl ring is not substituted by any substituents i.e. it bears hydrogen atoms only.

Preferred compounds of formula (I) within this set of embodiments include those wherein:

A and B each independently represent unsubstituted C_1 to C_6 alkylene;

K, D, Z and E each independently represent hydrogen, C₁-C₆ alkyl, phenyl, C₁-C₆ alkylphenyl or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J represents unsubstituted C₁ to C₆ alkylene; or two of K, D, Z and E together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from lower alkyl, phenyl or lower alkylphenyl.

R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl, phenyl or C₁ to C₆ alkylphenyl.

Further preferred compounds of formula (I) within this set of embodiments include those wherein:

A and B both represent -CH₂- or C₂H₄, particularly CH₂;

K, D, Z and E each independently represent hydrogen, C₁-C₆ alkyl, phenyl or C₁-C₆ alkyl or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J is the same as A; or two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form an unsubstituted phenyl ring;

R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl;

Still further preferred compounds of formula (I) within this set of embodiments include those wherein:

R¹ to R¹⁸ are the same and each represents C₁ to C₆ alkyl, particularly methyl.

Still further preferred compounds of formula I within this set of embodiments include those wherein:

K, D, Z and E are each independently selected from the group consisting of hydrogen or C₁ to C₆ alkyl, particularly where each of K, D, Z and E represent the same group, especially where each of K, D, Z and E represent hydrogen; or

K represents $-\text{CH}_2-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$ and D, Z and E are each independently selected from the group consisting of hydrogen or C₁ to C₆ alkyl, particularly where both D and E represent the same group, especially where D, Z and E represent hydrogen.

Especially preferred specific compounds of formula (I) within this set of embodiments include those wherein:

each R¹ to R¹² is the same and represents methyl;

A and B are the same and represent $-\text{CH}_2-$;

K, D, Z and E are the same and represent hydrogen.

In this particular set of embodiments, Ar may be defined as are "Ar" and "aryl" hereinafter, but preferably, Ar is defined as including six-to-ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups are optionally substituted with, in addition to K, D, E or Z, one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁷, C(O)SR²⁷ or C(S)NR²⁵R²⁶ wherein R¹⁹ to R²⁷ each independently represent hydrogen, aryl or lower alkyl.

(which alkyl group may itself be optionally substituted or terminated as defined hereinafter).

In a further set of embodiments, in a compound of either formula (I) or (Ia) at least one ($\text{CR}^x\text{R}^y\text{R}^z$) group attached to Q^1 and/or Q^2 , i.e. $\text{CR}^1\text{R}^2\text{R}^3$, $\text{CR}^4\text{R}^5\text{R}^6$, $\text{CR}^7\text{R}^8\text{R}^9$, or $\text{CR}^{10}\text{R}^{11}\text{R}^{12}$, may instead be congressyl or adamantyl, or both groups defined above as ($\text{CR}^x\text{R}^y\text{R}^z$) attached to either or both Q^1 and/or Q^2 , may, together with either Q^1 or Q^2 as appropriate, instead form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, preferably the at least one ($\text{CR}^x\text{R}^y\text{R}^z$) group being congressyl or adamantyl.

The adamantyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from lower alkyl, $-\text{OR}^{19}$, $-\text{OC}(\text{O})\text{R}^{20}$, halo, nitro, $-\text{C}(\text{O})\text{R}^{21}$, $-\text{C}(\text{O})\text{OR}^{22}$, cyano, aryl, $-\text{N}(\text{R}^{23})\text{R}^{24}$, $-\text{C}(\text{O})\text{N}(\text{R}^{25})\text{R}^{26}$, $-\text{C}(\text{S})(\text{R}^{27})\text{R}^{28}$, $-\text{CF}_3$, $-\text{P}(\text{R}^{56})\text{R}^{57}$, $-\text{PO}(\text{R}^{58})(\text{R}^{59})$, $-\text{PO}_3\text{H}_2$, $-\text{PO}(\text{OR}^{60})(\text{OR}^{61})$, or $-\text{SO}_3\text{R}^{62}$, wherein R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , R^{28} (defined as are R^{19} to R^{27} hereinbefore), lower alkyl, cyano and aryl are as defined herein and R^{56} to R^{62} each independently represent hydrogen, lower alkyl, aryl or Het. However, in one embodiment, the adamantyl groups are not substituted.

Suitably, when the adamantyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted C_1 to C_8 alkyl, $-\text{OR}^{19}$, $-\text{OC}(\text{O})\text{R}^{20}$, phenyl, $-\text{C}(\text{O})\text{OR}^{22}$, fluoro, $-\text{SO}_3\text{H}$, $-\text{N}(\text{R}^{23})\text{R}^{24}$, $-\text{P}(\text{R}^{56})\text{R}^{57}$, $-\text{C}(\text{O})\text{N}(\text{R}^{25})\text{R}^{26}$ and $-\text{PO}(\text{R}^{58})(\text{R}^{59})$, $-\text{CF}_3$, wherein R^{19} represents hydrogen, unsubstituted C_1 - C_8 alkyl or phenyl, R^{20} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} each independently represent

hydrogen or unsubstituted C₁-C₈ alkyl, R⁵⁶ to R⁵⁹ each independently represent unsubstituted C₁-C₈ alkyl or phenyl.

Suitably, the adamantyl group may comprise, besides hydrogen atoms, up to 10 substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Preferred substituents are unsubstituted C₁-C₈ alkyl and trifluoromethyl, particularly unsubstituted C₁-C₈ alkyl such as methyl. A highly preferred adamantyl group comprises hydrogen atoms only i.e. the adamantyl group is not substituted.

Preferably, when more than one adamantyl group is present in a compound of formula (Ia) or (I), each adamantyl group is identical.

The 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group (referred to as 2-phospha-adamantyl group herein) may optionally comprise, beside hydrogen atoms, one or more substituents. Suitable substituents include those substituents as defined herein in respect of the adamantyl group. Highly preferred substituents include lower alkyl, particularly unsubstituted C₁-C₈ alkyl, especially methyl, trifluoromethyl, -OR¹⁹ wherein R¹⁹ is as defined herein particularly unsubstituted C₁-C₈ alkyl or aryl, and 4-dodecylphenyl. When the 2-phospha-adamantyl group includes more than one substituent, preferably each substituent is identical.

Preferably, the 2-phospha-adamantyl group is substituted on one or more of the 1, 3, 5 or 7 positions with a substituent as defined herein. More preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3 and 5 positions. Suitably, such an arrangement means the phosphorous atom of the 2-phospha-adamantyl group is bonded to carbon atoms in the adamantyl skeleton having no hydrogen atoms. Most preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-phospha-adamantyl group includes more than 1 substituent preferably each substituent is identical. Especially preferred substituents are unsubstituted C₁-C₈ alkyl and trifluoromethyl, particularly unsubstituted C₁-C₈ alkyl such as methyl.

Preferably, 2-phospha-adamantyl represents unsubstituted 2-phospha-adamantyl or 2-phospha-adamantyl substituted with one or more unsubstituted C₁-C₈ alkyl substituents, or a combination thereof.

Preferably, the 2-phospha-adamantyl group includes additional heteroatoms, other than the 2-phosphorous atom, in the 2-phospha-adamantyl skeleton. Suitable additional heteroatoms include oxygen and sulphur atoms, especially oxygen atoms. More preferably, the 2-phospha-adamantyl group includes one or more additional heteroatoms in the 6, 9 and 10 positions. Even more preferably, the 2-phospha-adamantyl group includes an additional heteroatom in each of the 6, 9 and 10 positions. Most preferably, when the 2-phospha-adamantyl group includes two or more additional heteroatoms in the 2-phospha-adamantyl skeleton, each of the additional heteroatoms are

identical. An especially preferred 2-phospha-adamantyl group, which may optionally be substituted with one or more substituents as defined herein, includes an oxygen atom in each of the 6, 9 and 10 positions of the 2-phospha-adamantyl skeleton.

Preferably, the 2-phospha-adamantyl includes one or more oxygen atoms in the 2-phospha-adamantyl skeleton.

Highly preferred 2-phospha-adamantyl groups as defined herein include 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl group, and 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl group. Most preferably, the 2-phospha-adamantyl is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group or 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl group.

Preferably, when more than one 2-phospha-adamantyl group is present in a compound of formula (I) or (Ia), each 2-phospha-adamantyl group is identical.

The 2-phospha-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc of 901 Garner Road, Niagara Falls, Ontario, Canada L2E 6T4. Likewise corresponding 2-phospha-adamantyl compounds of formula (I) etc may be prepared by analogous methods.

Moreover, at least one of $\text{CR}^{13}(\text{R}^{14})(\text{R}^{15})$ and $\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$, when present, may instead be congressyl or adamantyl, optionally substituted as described above, or both groups defined as $\text{CR}^{13}(\text{R}^{14})(\text{R}^{15})$ and $\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$ attached to Q^3 , may together with Q^3 , instead form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, preferably the at least one of $\text{CR}^{13}(\text{R}^{14})(\text{R}^{15})$ and $\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$, when present, being congressyl or adamantyl.

Preferably, in a compound of formula (I) when both K represents $-\text{J}-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$ and E represents $-\text{J}-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$, then D represents $-\text{J}-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$.

By the term 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group we mean a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^1 , together with Q^1 to which they are attached, a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^2 , together with Q^2 to which they are attached, a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^3 , together with Q^3 to which they are attached, wherein Q^1 , Q^2 , or Q^3 is in the 2-position of the adamantyl group of which it forms an integral part and each of Q^1 , Q^2 , and Q^3 represents phosphorus.

Preferred compounds within the present set of embodiments and wherein at least one 2-phospha-adamantyl group is present include those wherein:

Groups $CR^1(R^2)(R^3)$ and $CR^4(R^5)(R^6)$ are attached to Q^1 , and the groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group;

Groups $CR^1(R^2)(R^3)$ and adamantyl are attached to Q^1 , and the groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group;

Groups $CR^1(R^2)(R^3)$ and congressyl are attached to Q^1 , and the groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group;

Two adamantyl groups are attached to Q^1 , and the groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group;

Two congressyl groups are attached to Q^1 , and the groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group;

The groups attached to Q^1 , together with Q^1 , form a 2-phospha-adamantyl group, and the two groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group.

Naturally, in the preferred compounds noted above, Q^1 and Q^2 can be interchanged, together with the groups attached thereto. Therefore, for example, the first preferred compound in the list could equally preferably be:

Groups $CR^7(R^8)(R^9)$ and $CR^{10}(R^{11})(R^{12})$ are attached to Q^2 , and the groups attached to Q^1 , together with Q^1 , form a 2-phospha-adamantyl group.

Highly preferred compounds within this embodiment include those wherein:

The groups attached to Q^1 , together with Q^1 , form a 2-phospha-adamantyl group, and the two groups attached to Q^2 , together with Q^2 , form a 2-phospha-adamantyl group.

Preferably, the groups attached to Q^1 are identical.

Preferably, the groups attached to Q^1 are identical, the groups attached to Q^2 are identical, and the groups attached to Q^3 are identical, more preferably, all such groups are identical or form with the Q they are attached to, identical groups.

Particularly preferred combinations in the present invention include those of formula (I) wherein:

- (1) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen;
 Q^1 and Q^2 both represent phosphorus.

- (2) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;

K represents $-\text{CH}_2-\text{Q}^3(\text{X}^5)\text{X}^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;

A and B are the same and represent $-\text{CH}_2-$;

Q^1 , Q^2 and Q^3 each represent phosphorus;

D and E are the same and represent hydrogen or unsubstituted $\text{C}_1\text{-C}_6$ alkyl, particularly hydrogen.

- (3) $(\text{CR}^7\text{R}^8\text{R}^9)$ and $(\text{CR}^{10}\text{R}^{11}\text{R}^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(\text{CR}^4\text{R}^5\text{R}^6)$ and $(\text{CR}^1\text{R}^2\text{R}^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
 K represents $-\text{CH}_2-\text{Q}^3(\text{X}^5)\text{X}^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;
 A and B are the same and represent $-\text{CH}_2-$;
 Q^1 , Q^2 and Q^3 each represent phosphorus.

In a further set of embodiments, in formula (I), Ar is a cyclopentadienyl group, and Z may be represented by $-\text{M}(\text{L}_1)_n(\text{L}_2)_m$ and Z is connected via a metal ligand bond to the cyclopentadienyl group, M represents a Group VIB or VIIIB metal or metal cation thereof; and L_1 represents a cyclopentadienyl, indenyl or aryl group each of which groups are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , OC(O)R^{20} , C(O)R^{21} , C(O)OR^{22} , $\text{NR}^{23}\text{R}^{24}$, $\text{C(O)NR}^{25}\text{R}^{26}$, $\text{C(S)R}^{25}\text{R}^{26}$, SR^{27} , C(O)SR^{27} or ferrocenyl;

L_2 represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

R^{43} to R^{48} each independently represent hydrogen, lower alkyl, aryl or Het;

$n = 0$ or 1 ;

and $m = 0$ to 5 ;

provided that when $n = 1$ then m equals 0 , and when n equals 0 then m does not equal 0 .

Preferably, A, B, Q^1 , Q^2 , K, D, E, and R^1 to R^{27} are as defined and described hereinbefore, including preferred embodiments thereof.

By the term "M represents a Group VIB or VIIIB metal" in a compound of formula I we include metals such as Cr, Mo, W, Fe, Co, Ni, Ru, Rh, Os, Ir, Pt and Pd. Preferably, the metals are selected from Cr, Mo, W, Fe, Co, Ni, Ru and Rh. For the avoidance of doubt, references to Group VIB or VIIIB metals herein should be taken to include Groups 6, 8, 9 and 10 in the modern periodic table nomenclature.

By the term "metal cation thereof" we mean that the Group VIB or VIIIB metal (M) in the compound of formula I as defined herein has a positive charge. Suitably, the metal cation may be in the form of a salt or may comprise weakly coordinated anions derived from halo, nitric acid; sulphuric acid; lower alkanolic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid,

fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluorinated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids derived from interactions between Lewis acids and Brønsted acids. Other sources which may provide suitable anions include the tetraphenyl borate derivatives.

Preferably M represents a Group VIB or VIIIB metal. In other words the total electron count for the metal M is 18.

Halo groups, which L_2 may represent and with which the above-mentioned groups may be substituted or terminated, include fluoro, chloro, bromo and iodo.

Suitably, if A represents cyclopentadienyl and $n = 1$, the compounds of formula I may contain either two cyclopentadienyl rings, two indenyl rings or one indenyl and one cyclopentadienyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "sandwich compounds" as the metal M or metal cation thereof is sandwiched by the two ring systems. The respective cyclopentadienyl and/or indenyl ring systems may be substantially coplanar with respect to each other or they may be tilted with respect to each other (commonly referred to as bent metallocenes).

Alternatively, when $n = 1$, the compounds of the invention may contain either one cyclopentadienyl or one indenyl ring (each of which ring systems may optionally be substituted as described herein) and one aryl ring (i.e. L_1 represents aryl) which is optionally substituted as defined herein. Suitably, when $n = 1$ and L_1 represents aryl then the metal M of the compounds of formula I as defined herein is typically in the form of the metal cation.

Suitably, when $n = 0$, the compounds of the invention contain only one cyclopentadienyl or indenyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "half sandwich compounds". Preferably, when $n = 0$ then m represents 1 to 5 so that the metal M of the compounds of formula I has an 18 electron count. In other words, when metal M of the compounds of formula I is iron, the total number of electrons contributed by the ligands L_2 is typically five.

Suitably, the metal M or metal cation thereof in the cyclopentadienyl compounds of formula I is typically bonded to the cyclopentadienyl ring(s) or the cyclopentadienyl moiety of the indenyl ring(s). Typically, the cyclopentadienyl ring or the cyclopentadienyl moiety of the indenyl ring exhibits a pentahapto bonding mode with the metal; however other bonding modes between the cyclopentadienyl ring or cyclopentadienyl moiety of the indenyl ring and the metal, such as trihapto coordination, are also embraced by the scope of the present invention.

Preferably, in the compound of formula I wherein Ar is cyclopentadienyl, M represents Cr, Mo, Fe, Co or Ru, or a metal cation thereof. Even more preferably, M represents Cr, Fe, Co or Ru or a metal cation thereof. Most preferably, M is selected from a Group VIIIB metal or metal cation thereof. An especially preferred Group VIIIB metal (M) is Fe. Although the metal M as defined herein may be in a cationic form, preferably it carries essentially no residual charge due to coordination with L₁ and/or L₂ as defined herein.

Preferably, when n = 1 in the compound of formula I, L₁ represents cyclopentadienyl, indenyl or aryl each of which rings are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, SR²⁷ or ferrocenyl (by which is meant the cyclopentadienyl, indenyl or aryl ring which L₁ may represent is bonded directly to the cyclopentadienyl ring of the metallocenyl group). More preferably, if the cyclopentadienyl, indenyl or aryl ring which L₁ may represent is substituted it is preferably substituted with one or more substituents selected from C₁-C₆ alkyl, halo, cyano, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴ where R¹⁹, R²⁰, R²¹, R²², R²³ and R²⁴ each independently represent hydrogen or C₁-C₆ alkyl.

Preferably, when n = 1, L₁ represents cyclopentadienyl, indenyl, phenyl or naphthyl optionally substituted as defined herein. Preferably, the cyclopentadienyl, indenyl, phenyl or naphthyl groups are unsubstituted. More preferably, L₁ represents cyclopentadienyl, indenyl or phenyl, each of which rings are unsubstituted. Most preferably, L₁ represents unsubstituted cyclopentadienyl.

In a particularly preferred embodiment of the present invention, in a compound of formula I, $n = 1$, L_1 is as defined herein and $m = 0$.

Alternatively, when n is equal to zero and m is not equal to zero in a compound of formula I, L_2 represents one or more ligands each of which are independently selected from lower alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$. More preferably, L_2 represents one or more ligands each of which are independently selected from C_1 to C_4 alkyl, halo, particularly chloro, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, wherein R^{43} to R^{48} are independently selected from hydrogen, C_1 to C_6 alkyl or aryl, such as phenyl.

In a particularly preferred alternative embodiment of the present invention, in a compound of formula I, $n = 0$, L_2 is as defined herein and $m = 3$ or 4 , particularly 3 .

M represents a metal selected from Cr, Mo, Fe, Co or Ru or a metal cation thereof;

L_1 represents cyclopentadienyl, indenyl, naphthyl or phenyl, each of which rings may be optionally substituted by one or more substituents selected from C_1 - C_6 alkyl, halo, cyano, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$, $NR^{23}R^{24}$;

L_2 represents one or more ligands each of which ligands are independently selected from C_1 - C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

$n = 0$ or 1 ;

and $m = 0$ to 4 ;

provided that when $n = 1$ then $m = 0$ and when m does not equal zero then $n = 0$.

Further preferred compounds of formula I include those wherein:

M represents iron or a cation thereof;

L_1 represents cyclopentadienyl, indenyl or phenyl group, each of which groups are optionally substituted by one or more substituents selected from C_1 - C_6 alkyl, halo, cyano, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$;

L_2 represents one or more ligands each of which are independently selected from C_1 - C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1 - C_6 alkyl or phenyl;

$n = 0$ or 1; and $m = 0$ to 4.

Still further preferred compounds of formula I include those wherein:

L_1 represents unsubstituted cyclopentadienyl, indenyl or phenyl, particularly unsubstituted cyclopentadienyl; and, $n = 1$ and $m = 0$.

Alternative preferred compounds of formula I include those wherein:

$n = 0$;

L_2 represents one or more ligands each of which are independently selected from C_1 to C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1 - C_6 alkyl or phenyl; and $m = 1$ to 4, particularly 3 or 4. For example, when $m=3$ the three ligands which L_2 may represent include $(CO)_2$ halo, $(PR^{43}R^{44}R^{45})_2$ halo or $(NR^{46}R^{47}R^{48})_2$ halo.

Particularly preferred combinations within this embodiment of the present invention and wherein at least one 2-phospha-adamantyl group is present include those of formula (I) wherein:-

- (4) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
 A and B are the same and represent $-CH_2-$;
 Q^1 and Q^2 both represent phosphorus;
 K represents hydrogen or unsubstituted C_1 - C_6 alkyl, particularly hydrogen;
 D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
 M represents Fe;
 $n = 1$ and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and $m = 0$.
- (5) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;

A and B are the same and represent $-\text{CH}_2-$;
 K, D and E are the same and represent hydrogen or unsubstituted $\text{C}_1\text{-C}_6$ alkyl, particularly hydrogen;
 Q^1 and Q^2 both represent phosphorus;
 M represents Fe;
 $n = 1$ and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and $m = 0$.

- (6) $(\text{CR}^7\text{R}^8\text{R}^9)$ and $(\text{CR}^{10}\text{R}^{11}\text{R}^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(\text{CR}^4\text{R}^5\text{R}^6)$ and $(\text{CR}^1\text{R}^2\text{R}^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
 K represents $-\text{CH}_2-\text{Q}^3(\text{X}^5)\text{X}^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;
 A and B are the same and represent $-\text{CH}_2-$;
 Q^1 , Q^2 and Q^3 each represent phosphorus;
 D and E are the same and represent hydrogen or unsubstituted $\text{C}_1\text{-C}_6$ alkyl, particularly hydrogen;
 M represents Fe;
 $n = 1$ and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and $m = 0$.
- (7) $(\text{CR}^7\text{R}^8\text{R}^9)$ and $(\text{CR}^{10}\text{R}^{11}\text{R}^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
 $(\text{CR}^4\text{R}^5\text{R}^6)$ and $(\text{CR}^1\text{R}^2\text{R}^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
 K represents $-\text{CH}_2-\text{Q}^3(\text{X}^5)\text{X}^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;

A₁ and A₂ are the same and represent -CH₂-;

Q¹, Q² and Q³ each represent phosphorus;

D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

M represents Fe;

n = 1 and L₁ represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and m = 0.

Suitably, the process of the invention may be used to catalyse the hydroformylation of an ethylenically unsaturated compound in the presence of carbon monoxide and hydrogen, i.e. the process of the invention may catalyse the conversion of an ethylenically unsaturated compound to the corresponding aldehyde. Conveniently, the process of the invention will show an increased selectivity to the linear aldehyde product, compared to the branched aldehyde product, in comparison with similar processes but where the chlorine moiety is not present. Preferably, the ratio of linear:branched product obtained from the hydroformylation process is greater than when using comparable catalyst systems/solvents but wherein a chlorine moiety is not present, i.e. the ratio is biased towards the linear product, more preferably the linear:branched ratio is greater than 1:1, more preferably is greater than 1.25:1, even more preferably is greater than 1.5:1, yet more preferably is greater than 2:1, most preferably is greater than 3:1.

Conveniently, the process of the invention may utilise highly stable compounds under typical hydroformylation reaction conditions such that they require little or no

replenishment. Conveniently, the process of the invention may have an increased rate of the hydroformylation reaction of an ethylenically unsaturated compound compared to known processes. Conveniently, the process of the invention may promote high conversion rates of the ethylenically unsaturated compound, thereby yielding the desired product in high yield with little or no impurities. Consequently, the commercial viability of the hydroformylation process, such as the hydroformylation of an ethylenically unsaturated compound, may be increased by employing the process of the invention.

The following definitions apply to all sets of embodiments noted hereinbefore and where applicable, unless otherwise stated.

The term "Ar" or "aryl" when used herein, and unless otherwise indicated, includes five-to-ten membered, preferably six-to-ten-membered carbocyclic aromatic or pseudo aromatic groups, such as phenyl, ferrocenyl and naphthyl, preferably phenyl and naphthyl, which groups are optionally substituted with, in addition to K, D, E or Z, one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below).

Suitably, when Ar or aryl is cyclopentadienyl and when D and E together with the carbon atoms of the

In this case, it was found that there was 10% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an l:b ratio of 4:1.

Example 7

Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor

Details were as in Example 5 above, except 10ml of toluene was used as the solvent.

In this case, it was found that there was 11% conversion to the aldehyde product, with 100% selectivity to linear nonanal.

Comparative Example 2

Hydroformylation of 1-octene: Chlorine moiety not present

Details were as in Example 4 above, except 10ml of toluene was used as the solvent.

In this case, it was found that there was 89% conversion to the aldehyde product, with only 50% selectivity to linear nonanal, an l:b ratio of 1:1.

Examples 4-7 clearly show the increase in selectivity towards the linear product over the branched product, from the hydroformylation of 1-octene, when chlorine moiety is present in the solvent (Example 4), the rhodium precursor (Examples 6 and 7), or both the solvent and the rhodium precursor (Example 5), compared to Comparative Example 2, where no chlorine moiety is present, either in the rhodium precursor or in the solvent.

Although a few preferred embodiments have been shown and described, it will be appreciated by those skilled in the art that various changes and modifications might be made without departing from the scope of the invention, as defined in the appended claims.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any

accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.